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ABOUT AEROSOLS, WITH EMPHASIS ON THOSE OF IRON OXIDE (UEBER AER--ETC(U)
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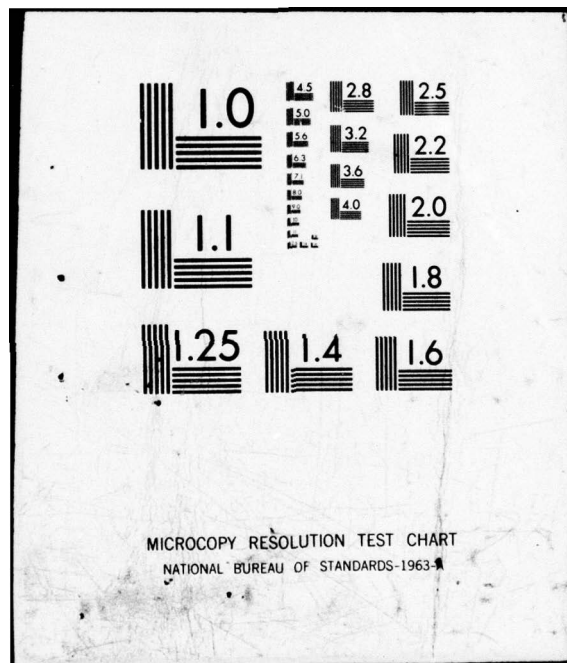
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1. The viewpoints predominant up to now in the investigation of aerosols.

It is known that the characteristics of colloidal systems depend to the greatest extent upon the conditions of formation. With the hydrosols condensation methods and dispersion methods differ sharply, depending on the material which has been transformed into the dispersed state, producing first the monomolecular crystalloid dissolved state or a compact, adherent form.

It is always very difficult to obtain a hydrosol of constant and reproducible characteristics by means of a dispersion method, because on the one hand the mechanical approach with which the colloidal particles are separated from the compact mass cannot be kept completely constant, and on the other hand, the material that is to be dispersed also possesses inhomogeneities. Because of this, colloidal solutions whose properties vary extraordinarily from case to case and are nonuniform with respect to their particle sizes are obtained. As an example of this the Bredig procedure for preparation of noble metal hydrosols may be mentioned.

Results are different when condensation procedures are used. It has been the great service of R. Zsigmondy 1) to be the first to produce very good reproducible gold hydrosols by reduction of gold salt solutions, and to have identified their characteristics by systematic studies. From this there resulted very much, generally useful knowledge about the colloidal state.

The conditions in other, nonliquid dispersion colloidal systems, as for example, aerosols, are analogous. For studying aerosols it is thus likewise

obvious to try to prepare pure condensation colloids and study their characteristics.

There is not such a large number of purely scientific publications on colloidal systems, with gaseous dispersion media, as there are, for example, for hydrosols. The reason for this is the fact that it is really difficult to produce well reproducible colloidal systems of dispersed fog or dust. The less volatile the material to be dispersed is, the less easy it is to prepare pure condensation aerosols. For instance, the attempt has been made to prepare aerosols from the extremely high boiling metallic oxides so that the particular metal itself was evaporated in the electric arc. The vapors then reacted with the oxygen of the air, and thus yielded the corresponding metal oxide aerosol 2). However, with this procedure there is always not only a pure vaporization occurring at the electrodes, but also there is some possibility that larger particles from the electrode material will be entrained, similarly to when noble metal hydrosols are prepared by underwater sparking.

Another method of preparation of condensation aerosols is the reaction between gaseous starting materials, as for example the reaction of ammonia with hydrochloric acid gas for ammonium chloride aerosols, or that of sulfur dioxide with oxygen for sulfur trioxide aerosols 3). However, so many-fold high concentrations have been used with these that the individual particles of the aerosol formed, because of their sizes (10^{-12} g) tended toward marked sedimentation. Furthermore, the concentrated aerosols formed in this way are also nonuniform, because the mixture of the two reactant, gas forming components is not entirely homogeneous, and concentration of the reaction product at separate spots throughout the aerosol cannot be avoided. More recently, English investigators 4) have tried primarily to prepare condensation aerocolloids according to various methods, and explain their course of

aggregation according to the theory of von Smoluchowski 5). The German investigators -- starting from meteorological problems -- have been occupied primarily with the investigation of water vapors and are trying to evaluate the practical results of their studies for meteorology 6). Primarily, these studies relate to the question of how stabilizing the electrical charge is on the cloud particles.

Thus, it can certainly be said that it is just lately that a proportionately not very large number of works have tried to comprehend the nature of the aerosols formed according to condensation procedures, starting from purely scientific viewpoints. However, very frequently because of an overwhelming practical interest the characteristics of naturally occurring aerosol systems (cloud, dust, smoke) have been studied.

II. Some general characteristics of condensation aerosols.

The aerosols essentially differ from all other colloidal systems by their greater instability. Their particle number decreases markedly above all shortly after preparation. This is based on two events, the enlargement by aggregation, and the sedimentation of the colloidal particles 7). Although the type of the process of aggregation is not essentially different between condensation aerosols and dispersion aerosols, the process of sedimentation in the two types of aerosols proceeds entirely differently. The chronological course of sedimentation expresses itself in the decrease in concentration of the aerosol under consideration. The decrease of the entire mass dispersed as an aerosol as a function of time is a good criterion of the uniformity or nonuniformity of an aerosol. Curve I of Fig. 1 shows the characteristic curve of decrease in mass of a uniform cloud, and Curve II shows that of a non-uniform cloud.

While a uniform aerosol has a curve form concave to the coordinate axes, for the nonuniform cloud the initially convex form of the curve is typical. The marked concentration decrease of nonuniform clouds after their production is due to the fact that the coarse particles, having a large mass and thus a high velocity of fall, sediment out relatively rapidly. Only when the very largest and also the rather less large particles have fallen out does the cloud gradually become increasingly uniform, and the curve of decreasing concentration changes over into the decrease curve of an aged, uniform aerosol.

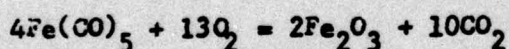
The concentration decrease of a uniform cloud is least right after preparation. Then though the sedimentation increases with time, because larger particles with a greater sedimentation tendency gradually form by aggregation. After a certain time the concentration decrease curve for a uniform cloud shows a constant, almost linear decrease. This constant progress of the sedimentation has also been observed by H. Remy 8), who studied the fall of the upper cloud boundary primarily in ammonium chloride clouds. The slope of these constantly falling curve segments depends essentially on the form and weight of the individual sedimenting particles. These in their turn will be affected primarily by the concentration and type of substance in the aerosol. Observation of the sedimentation comprises, among other things, a means of examining the uniformity of a cloud.

By the concept of uniformity in an aerosol it should not be understood that every particle has precisely the same size and form. That is something which, as a matter of fact, is scarcely possible, because actually an aerosol undergoes constant change. An aerosol then can be designated as uniform if the by far largest number of particles do not essentially differ in their size. If the frequency of the individual particle sizes of a

"uniform" aerosol were represented graphically as a function of the particle sizes actually present, then a curve with a definite maximum would result. The velocity of gas molecules has a similar frequency distribution. It should be thoroughly understood now that a uniform aerosol is obtained when the substance concerned is present in the gas or vapor form. Eliminating the possibility of error, this means then that in the sense discussed here a formed condensation cloud must always be uniform.

III. Colloidally dispersed iron oxide dusts that arise from the photoexposure of iron pentacarbonyl vapor diluted with air.

We have searched for a suitable, easily reproducible system for the present study of uniform aerosols. We found all of the required characteristics confirmed best by colloidally dispersed iron oxide dusts which arise from the photoexposure of a mixture of a little iron pentacarbonyl with an excess of air. Under the action of ultraviolet as well as visible light rays the iron pentacarbonyl vapor then decomposes in the presence of atmosphere oxygen about according to the equation:



We have not studied the course of this gas reaction in further detail; we have been satisfied just to ascertain that under the research conditions that we selected ferric oxide is the single solid end product of the reaction between the once gaseous components.

We undertook the study in large 10 to 15 liter capacity flasks. The concentration of the pentacarbonyl was varied in order that between 10 and 100 mg of Fe_2O_3 could be formed per cbm. In order to be able to accurately adjust the lower concentrations, the iron pentacarbonyl was dissolved in absolutely dry, chemically pure ether, and measured amounts of this solution

of known concentration were added to the experimental flasks. After the ether and pentacarbonyl were evaporated, the flask contents were shaken and mixed long and carefully. To make sure that there was an all-round, even exposure to irradiation the flask was placed on a rotating bracket and continuously rotated during the irradiation, which was carried out by a carbon arc lamp with a 20 ampere load. The distance from the crater of the carbon arc to the forward edge of the flask amounted to about 15 cm. Through a fairly great number of experiments we naturally determined right away how long various concentrated mixtures of pentacarbonyl vapor reacted quantitatively with how much air according to the schematic formulation already given.* It

* The genesis of the iron oxide aerosol can be carried out and, beyond this, also be demonstrated. If the mixture of air with a little pentacarbonyl vapor is introduced into the illuminated chamber of a focused microscope, then at first only an absolutely dark field is visible. After a little time, though, a huge number of the very smallest luminous particles suddenly are seen, which are in very vigorous motion. Gradually the number of particles decreases, the light intensity becomes stronger, and their movements become slow and sluggish.

was found that under our experimental conditions after a 5 to 6 minutes irradiation all mixtures of air with a little pentacarbonyl vapor are transformed quantitatively,** yielding a concentration of up to 250 mg per cbm.

** The reaction, which is induced by the irradiation, does not proceed further in the dark. The amount of light irradiated can be conveniently measured by the amount of iron oxide separated out.

All of the iron oxides used in what follows have been prepared by a 5-6 minute irradiation.

Now it was tested whether the ferric oxide aerosols prepared this way tallied with all requirements of equivalence. Equal amounts of pentacarbonyl were evaporated and all of the iron oxide dust colloiddally dispersed in the gas space was measured analytically each time after ageing periods of various lengths. The analytical measurement took place with the aerosol being precipitated by suction onto a dense cotton filter, and brought into solution with 1N hydrochloric acid. Its iron content was compared colorimetrically with that of a standard iron solution, eliminating the possibility of error, according to the thiocyanate method. Fig. 2 shows the mass decrease curve obtained for an iron oxide aerosol of 20 mg per cbm. The amount of dust is read on the ordinate, and the age of the aerosol is read off of the abscissa.

We see that the path of the curve corresponds completely to that for an uniform condensation aerosol. The initially constant amount of colloiddally dispersed iron oxide dust shows later an almost constant decrease.

The course of aggregation of the single particles in such ferric oxide condensation aerosols as a function of time and concentration were then studied. We made use of a simple split ultramicroscope in which it was seen to that the lead-in path for the observation chamber was as short, broad, and without very sharp bends as possible. The mean value of the results of these studies are shown as curves in Fig. 3. For the individual counts we removed from the aerosol every time only so much, so that the total concentrations remained practically constant during the experiment.

The paths of the curves which were obtained at the four selected concentrations of 12.5, 25, 50, and 100 mg of Fe_2O_3 per cbm are definitely

quantitatively different, but qualitatively they are of the same type. During the first 30 minutes of the lifetime of the aerosol a very marked decrease in the number of particles is evident in the volume counted. After about 30 minutes, this decrease becomes less, until becoming quite small after 50-60 minutes. Then the aggregation proceeded extremely slowly because, on the one hand, the number of particles had dropped very low and thus the frequency of collision between individual particles had become smaller, and also because the mobility of these individual particles had decreased as a result of the particle enlargement. This is shown particularly well in the following graphical diagram. Thus, Fig. 4 shows the mean mass of the individual particles as a function of the aerosol age. It is apparent that after about 60 minutes the mean mass of the individual particles of the aerosol then increases extremely slowly, and has become almost constant. On the basis of concentration, it amounts to between 12×10^{-15} and 40×10^{-15} g, thus being quite unusually much less than the mean particle size of Remy's ammonium chloride aerosols previously reported. Therefore Fig. 4 is more clear, because in this sort of graphic representation the individual curves present do not cross over.

Now, if the weights of the individual particles, which were reached after 60 minutes, and their relationship at that time with the concentration of the particular aerosol are compared with one another, the conditions which result are illustrated by curve I in Fig. 5. On the x-axis (below it) is the aerosol concentration, and on the ordinate the mean weight of the individual particles is shown in units of 10^{-15} g. In its upper portion curve I is practically a straight line. In the same concentration range the mean weight of the individual aerosol particles is a linear function of the concentration.

Below an aerosol concentration* of about 20 mg Fe_2O_3 per cbm, this linear

* In the curve I of Fig. 5 the final particle weight for the aerosol concentration of 6.6 mg of Fe_2O_3 per cbm is shown as that which can be reached by extrapolation of the curve of Fig. 6 (following series of studies) to the gas pressure of 750 mm.

relation does not hold anymore, as is apparent. When the aerosol concentration falls, the mean particle weight decreases more and more. The validity of the linear relation mentioned is certainly limited in going upward. In the range of very high aerosol concentrations even after a very long aerosol lifetime the aggregation would still have a quite measureable value. All of these studies show that it is entirely possible to prepare uniform condensation aerosols of a definite particle size reproducibly by appropriate choice of the concentration of iron oxide!

In order to study the factors which affect the type and size of aggregation still further, we investigated the dependence of the particle number and the mass of the individual particles on the gas pressure of the aerosol system. Kohlschuetter* has reported concerning this that the particle

* Locus cited

enlargement must proceed much faster with decreased pressure than at normal gas pressure. In our studies we proceeded by smashing the ethereal iron pentacarbonyl solution -- sealed in thin walled glass vials -- inside the more or less well evacuated flasks. The vials were destroyed by shaking; their contents evaporated immediately. Then the low pressure of the

air-ether mixture was measured. After the irradiation we allowed the aerosol systems which this time all had the constant concentration of $6.6 \text{ mg Fe}_2\text{O}_3$ per cbm, to age exactly one hour, though without change in gas pressure. It was filled with air up to normal gas pressure, then in a well known procedure the mean particle number was measured in a counting chamber, and the mean weight of the individual particles was calculated by concentration measurements. The curve in Fig. 6 shows the experimental results graphically, and shows that within the range of pressure studied the mean particle number of a particular aerosol volume (for example of $10^6 \mu^3$) is practically directly proportional to the gas pressure of the aerosol system -- or expressed otherwise -- the number of gas molecules of the dispersion medium. Of course, a precondition for this is that only uniform condensation aerosols with the same iron oxide concentration will be compared with each other

Because the viscosity of a gas is independent of pressure over wide ranges*, then indeed only the greater probability with which aerosol particles

* The viscosity drops sharply with the pressure only in a high vacuum.

themselves can collide is vitally important for the more marked decrease of the particle count in aerosol systems under reduced pressure. At an identical aerosol concentration this probability decreases linearly with increasing numbers of gas molecules of the dispersion medium, and with increasing gas pressure of the aerosol system.

If the mean particle weight is plotted as a function of gas pressure, a hyperbolic curve results, as shown by curve II in Fig. 5 (upper legend of the x-axis!). With a constant iron oxide concentration the mean particle weight of the uniform condensation dust also becomes smaller with increasing gas

pressure of the aerosol system along a hyperbolic curve. By properly controlling the gas pressure of the aerosol system, and with a given iron oxide concentration uniform condensation aerosols with a desired particle size can be reproducibly generated.

IV. The electrical charge of the aerosol particles.

The question whether the electrical charge of the individual particles exerts a stabilizing effect on the system of an aerosol in a manner similar to what is the case with hydrosols has already been of interest from an early time. It has been found that the aerosols which are formed by a chemical reaction from gaseous components are charged initially 14), and that the small, spontaneously (?) created electrical charge is certainly of underestimated significance for stability.

Ahrend and Kallmann 15) have studied the electrical charge of aerosol particles in an ionic atmosphere by ion absorption. They came to the conclusion that the number of elemental charges is proportional to the particle weight. For large particles (radius greater than 10^{-4} cm, particle weight greater than 10^{-12} g) the number n of the elemental charges frequently can be very large (n greater than 1,000). Wigand and Frankenberger 16) have carried over the theory of Ahrend and Kallmann to the naturally occurring smoke clouds. They have found that heavily synonomously charged clouds are very much more stable and less inclined to leave off settling than clouds with little or no charge.

Recently systematic investigations of the electrical charge of individual particles in various clouds have been published by H. Sachse 17). He obtained results similar to those of Ahrend and Kallmann. The most varied methods of preparation were used by H. Sachse for producing the aerosols.

Almost all of these studies have been conducted in aerosols with moderately coarse individual particles. In connection with our work the interest were questions of how high the charge of a uniform aerosol with very small individual particles (weight about 10 to 50×10^{-15} g) would be, how it would be constituted, and also whether an essentially stabilizing effect on the aerosol system by the electrical charge could be discerned. We also wanted to investigate whether and how the electrical charge of the particles changes with the age of the aerosol system.

The individual particles of a hydrosol are -- apart from some special cases -- electrically charged, and are unequivocally only either positive or negative. The situation is entirely different with condensation aerosols. Right after their preparation pure condensation aerosols are uncharged, and charges appear only during the course of their aging. Thus, the charges that appear in diluted aerosols seem to have none or only a slight effect on the stability of the aerosol. The magnitude of these charges is naturally only extremely small. But the important question that results now is whether aerosols can be stabilized by unequivocal, forced charge. This question will be treated in the later sections. However, first of all, the spontaneous (?) charge of the ferric oxide aerosols is to be described.

Even if they are uncharged at the beginning, all iron oxide aerosols acquire electrical charge. Two types of charging appear in an equal amount. We do not desire to make any comments about the origin of these charges, because no unequivocal explanation has resulted from our studies. In Fig. 7 following, the sequence of charging is schematically represented. Curve I shows (left ordinate) the course of aggregation of an iron oxide aerosol as a function of time, and curve II shows the ascent of the electrical charge of the individual particles as percentages of the total particle number

(right ordinate). At the beginning, while only about 15 per cent of the particles are charged, about 80 percent have an electrical charge after two hours. Finally, further along in time the per cent value of individual charged particles increases scarcely at all.

The measurement of the electrical charging was carried out with two oppositely located sides of the observation chamber of the ultramicroscope provided with condensor plates. The distance between the condensor plates amounted to 0.4 cm; the voltage imposed was 220 volts. The number of particles located in a definite volume was then counted, and how many of them drifted to the positive and negative condensor plates when the power was turned on were counted. Naturally, each time the mean was obtained from a large number of individual measurements.

We have applied ourselves to the question of whether it is possible to elicit an unequivocal positive or negative charge by an electrical point discharge of an electrical high voltage source either by the positive brush discharge or the negative glow discharge. While studying this question we found at first that a marked change in the particle number occurred if an induction coil with a very high voltage of 50,000 volts was used. Within a very brief time the individual particles of the aerosol were driven to the walls of the vessel and absorbed there. When the study was repeated with lower voltages of about 20,000 volts the result, though, was that even with a two minute longer treatment and after allowing the sample to stand for a more extended time (two hours ageing time) 70 per cent of the original amount of the aerosol present was still present. Thus, with the much milder type of charging the largest part of individual aerosol particles remained.

As a result of this study it was evident that it is completely possible to obtain unequivocally positively or negatively charged aerosols, and that

each time then at the beginning almost 100 per cent of the aerosol particles were negatively charged if the glow discharge of the induction coil had been used for the charging; besides that there was only a vanishingly small percentage of positive particles present. However, this condition was changed by allowing the aerosol to stand so that while the number of negatively charged particles constantly decreased, the number of the particles that were positive increased. After about five hours positively and negatively charged particles were present in about the same amounts. At that time the total charge was decreased by 80-90 per cent. We found similar results when we used the positive brush discharge of the induction coil instead of the negative discharge. The charging condition was then reversed. At first almost only positive particles were present. Fig. 8 following shows schematically the conditions described with an initially positively charged iron oxide aerosol.

In the individual studies charging was carried out for various times: $\frac{1}{2}$, 1, and 2 minutes. The type of charging was always the same. Only the particle number seemed to decrease at the longer durations of charging. With the equipment which was available to us initially we could not ascertain exactly the actual number of elemental charges there are present on a particle, but in correspondence with the small size of the particles (weight about 10 to 20×10^{-15} g), the charges did not seem to be essentially greater than unity.

Although it could be properly assumed that aerosols of this type have a considerably longer duration of life, and are much stabler because of their synonomous charge, there was no indication for this. The curves characteristic of aerosols with and without forced electrical charging are almost identical. However, this conflicts with the fact that after about five hours the state of the electrical charge becomes entirely equivalent in two types of aerosol.

However the iron oxide aerosols may be prepared and pretreated, they are ultimately up to 80-90 per cent charged and possess about the same amounts of positively and negatively charged individual particles.

Summary.

After a review of the viewpoints which up to now have been predominantly standard, several general characteristics of condensation aerosols were described. After that, the properties of colloiddally dispersed iron oxide dust which forms during irradiation of mixtures of a little iron pentacarbonyl vapor and excess air were discussed. The relationship of the mass of individual particles to the concentration and gas pressure of the aerosol system, and in addition the electrical characteristics of aerosols, which were either spontaneously ~~(?)~~ charged or which were given a charge by a physical induction were set forth.

